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Abundances of Volatile-Bearing Phases in Carbonaceous Chondrites and Cooling
Rates of Meteorites Based on Cation Ordering of Orthopyroxenes

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The "deliverables" for the grant received during this period are (1) a comprehensive proposal for work during the period 3/1/89 to 2/28/90 and (2) results of preliminary calculations of volatile abundances in carbonaceous chondrites.

Both objectives have been met. The results of the calculations of the volatile abundances will be presented at the Ninth SSI Princeton Conference on Space Manufacturing, May 11, 1989. In addition, the method (Ganguly 1982) has been refined for the calculation of cooling rate on the basis of cation ordering in orthopyroxenes, and it has been applied to the derivation of cooling rates of some stony meteorites. Evaluation of cooling rate is important to the analysis of condensation, accretion, and post-accretionary metamorphic histories of meteorites. The method of "orthopyroxene speedometry" is widely applicable to meteorites and would be very useful in the understanding of the evolutionary histories of carbonaceous chondrites, especially since the conventional metallographic and fission track methods yield widely different results in many cases. The results will be presented at the Lunar and Planetary Science Conference XX, 1989. The following abstracts summarize the major conclusions of the volatile abundance and cooling rate calculations.

Theoretical Predictions of the Nature and Abundances of Volatile Bearing Phases in Carbonaceous Chondrites,
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The overwhelming majority of asteroidal bodies consist of carbonaceous chondrites. Thus, the study of carbonaceous chondrites is very important to the assessment of resource potentials of near-earth asteroids. The carbonaceous chondrites are important potential resources for volatiles which may be used for fuels and propellants. The volatiles are stored in the minerals as structurally bound components in the organics, and in the possible cometary cores. The hydrous minerals have been characterized as a mixture of phyllosilicates, but further characterizations by conventional methods have proved to be extremely difficult due to the extremely fine-grained nature of the material. However, these phases need to be properly characterized if we are to efficiently release their volatiles for practical uses.

In this work, we have calculated at several P-T conditions the nature and abundance of the volatile bearing phases by minimizing the Gibbs free energy (G) of the system Mg-Fe-Al-Si-C-H₂-O₂, constrained by the bulk composition of the Orgueil CI chondrite. The minimization was carried out using the method of Lagrangian multiplier and a thermochemical data base consisting of about 100 minerals and 70 vapor species. Further, the effects of solid solutions (ideal and nonideal) have been taken into account. Due to the lack of adequate data, we have assumed that the phyllosilicates behave as ideal solutions.

The results show that a minimum pressure of about 1 bar at 500 K is needed to form the hydrous phases and that the primary hydrous minerals are antigorite and talc. Some amount of chlorinochlore (~ 2 mol%) may also be present. The amount of water structurally bound in the minerals should be about 5-10 wt% of the condensed inorganics. The amount of crystalline graphite may be very small, within a few mol%. There is also abundant magnetite. The relatively high pressure required to form the hydrous phases could preclude their formation by direct condensation from solar gas.

The vapor phase in equilibrium with these crystalline phases consists primarily of H₂O (~ 70 mol%), CH₄ (~ 20 mol%), and CO₂ (~ 10 mol%). This may be an approximate composition of the possible cometary core if we assume that the core represents the trapped volatiles, the composition of which was controlled by reaction with the minerals and other condensed phases.

There are considerable uncertainties in the thermochemical data of the phyllosilicates, especially of the Fe-end members and in the thermodynamic mixing properties of their Fe-Mg joins. Thus, the above results must be treated with caution. Further studies on the refinement and systematization of the thermochemical properties are in progress. Also, we need to take into account sulfur and organics in free energy minimization calculations to develop a more reliable model of the mineralogical characteristics of carbonaceous chondrites. This work is to be published in the Proceedings of the May 1989 SSI Conference (Appendix E).

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Fe²⁺-Mg Ordering in Orthopyroxenes and the Cooling Rates of Meteorites, Jibamitra Ganguly and Kunal Bose, Department of Geosciences, University of Arizona, and Subrata Ghose, Department of Geological Sciences, University of Washington

The cooling rates of meteorites have been a subject of central importance in the understanding of their origin and evolution. However, the commonly used methods for the determination of cooling rates of meteorites often yield conflicting results. A potentially powerful recorder of the cooling rates is the state of Fe-Mg ordering in

orthopyroxenes (OPx), which can be found in any stony and stony-iron meteorite, and as silicate inclusion in some iron meteorites. However, despite its many applications in terrestrial problems, this method has not yet been used to derive quantitative constraints on the cooling rates of meteorites.

The "cation-ordering speedometry" involves reconstruction of the ordering state of a sample at its peak temperature and numerical simulations of the change of site occupancies as a function of cooling rate (Ganguly 1982). A substantial amount of thermodynamic and kinetic data, which are required for these calculations, is available in the literature (Ganguly 1982, Anovitz, et al. 1988). An example of the simulated evolution of M2 site occupancy is shown in Figure 2.3, using an OPx from the Steinbach meteorite for which the measured $X_{Fe(M2)} = 0.304$ [$X_{Fe} = Fe^{2+}/(Fe^{2+} + Mg)$]. The cooling is assumed to follow the form $1/T = 1/T_0 + nt$, where T_0 is the peak temperature and n is a cooling time constant. The observed site occupancy is exactly reproduced as the quenched ordering state in a simulated evolution, which is characterized by T-t path with $n = 1.5(10^{-12}) \text{ yr}^{-1}$. Similar calculations are carried out for orthopyroxenes from Shaw and Johnstown meteorites (Table 2.2). The cooling rates, given by nT^2 , are strictly applicable around the closure temperatures (T_c) and are quite insensitive to errors in the estimation of T_0 . Any other cooling law can also be used.

Figure 2.4 shows the effect of cooling rates on quenched M2 site occupancy for three bulk X_{Fe} values. For comparison, all $X_{Fe(M2)}$ values are relative to those for a cooling rate of 150°C/my for the different bulk compositions. It is clear that the retrieved cooling rates are very sensitive to errors in the determination of site occupancies of natural samples, especially for Fe-poor compositions. A precision of 0.002 in the site occupancy determination is a difficult but attainable goal in single crystal X-ray analysis. This will limit the precision of the retrieved cooling rates of meteoritic orthopyroxenes to a factor of 5-10, depending on the composition and cooling rate.

The site occupancies of the meteoritic orthopyroxenes used in this work lack the high precisions required for reliable cooling rate calculations. Nonetheless, it is important to note that, despite their uncertainties, the inferred cooling rates for Shaw and Steinbach orthopyroxenes are in good agreement with those derived from metallographic properties of these meteorites (Taylor et al. 1979, Reid et al. 1974). In contrast, the ^{24}Pu track records were used to derive (Pellas and Storzer 1977, Pellas et al. 1978) a cooling rate for the Shaw meteorite below 350°C , which is three orders of magnitude slower than that shown in Table 2.2. Thus, either there was a drastic change of cooling rate of the Shaw meteorite between 400 and 350°C , or the ^{24}Pu result

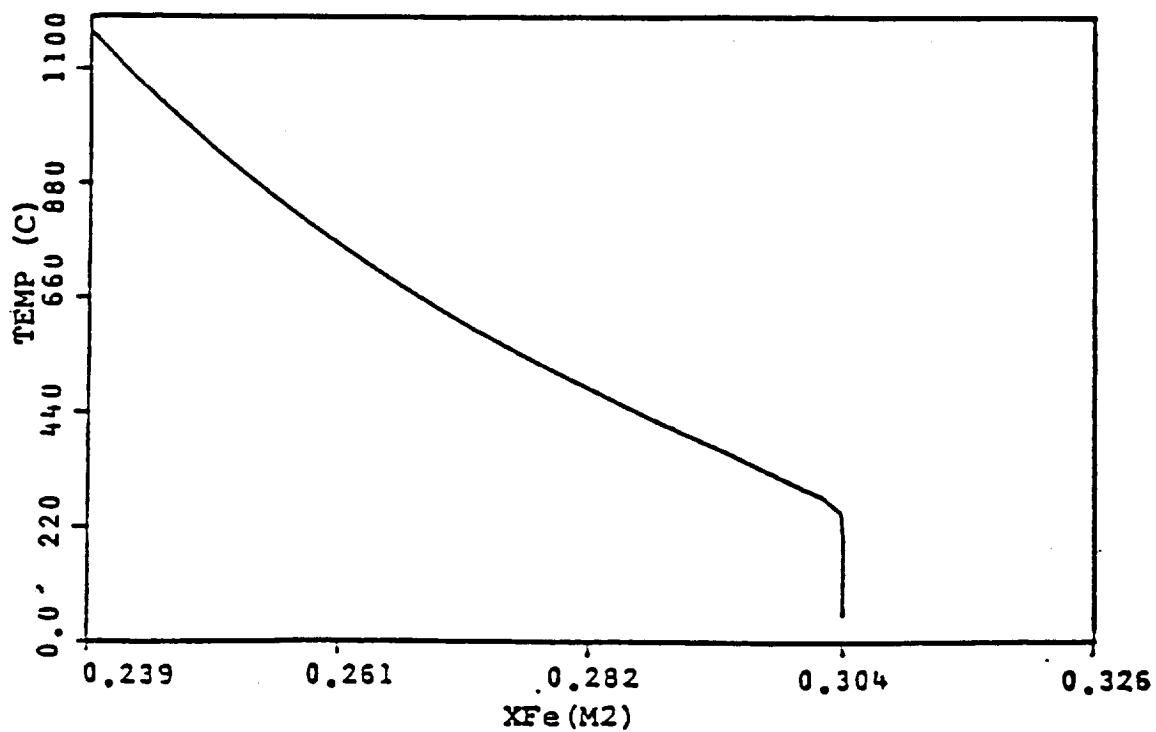


Figure 2.3

Table 2.2. Summary of cooling rate calculations of meteoritic orthopyroxenes.

Sample	Fe ²⁺ / (Fe ²⁺ + Mg) Total	M2	T _c (°C)	n, yr ⁻¹	(dT/dt) _{T_c} , °C/my	Site Occupancy Measurement
Johnstown	0.175	0.324	400	4E-9	1.8E3	X-ray (Dodd et al. 1975)
Steinbach	0.161	0.304	304	1.5E-12	0.5	X-ray (Reid et al. 74)
Johnstown	0.237	0.451	318	1.5E-12	0.5	X-ray ^a

^aPreliminary results from this work.

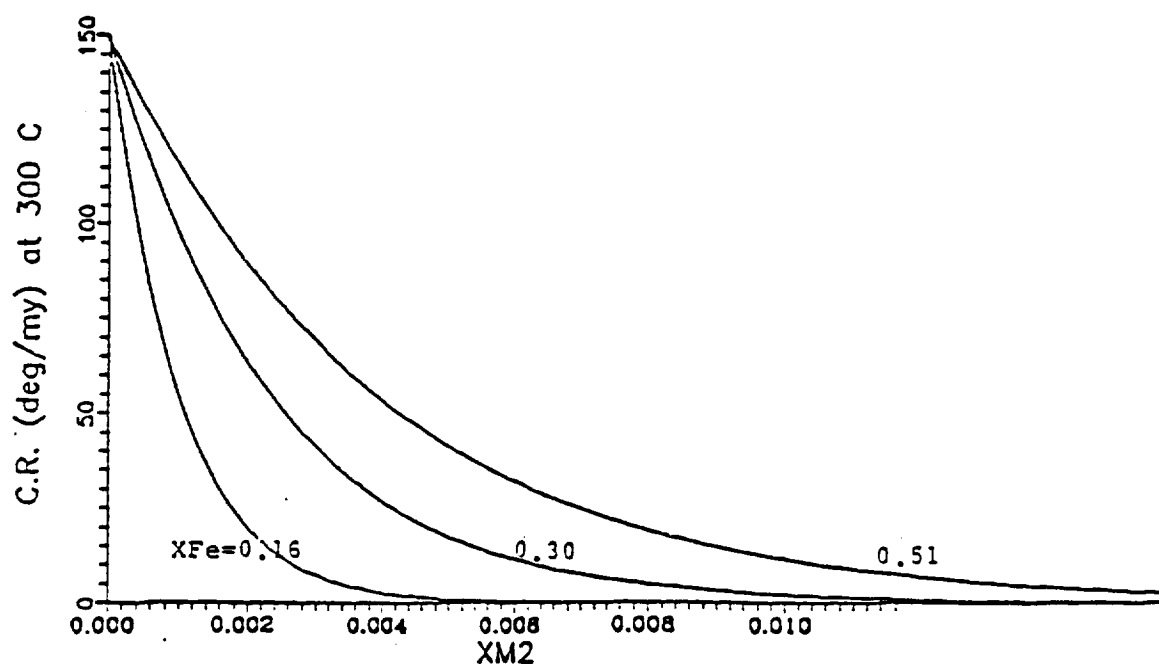


Figure 2.4

requires a careful reevaluation. Although the Johnstown meteorite is shocked (Mori and Takeda 1981), the high degree of Fe-Mg order in OPx suggests that the magnitude of shock was <450 Kb (Dundon and Hafner 1971). These results illustrate the potential applications and importance of the "cation ordering speedometry," which should be most widely applicable in the study of cooling rates and shock histories of meteorites owing to the widespread occurrence of orthopyroxenes.

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